Oxygen K Edge Total Electron Yield Spectra

M. Uda[1,2], T. Yamamoto[1], H. Osawa[2], T. Tatebayashi[2], A. Kanai[2], H. Wakita[3],
K. Taniguchi[4], J. H. Underwood[5] and R. C. C. Perera[5]

[1]Laboratory for Materials Science and Technology, Waseda University,
Nishiwaseda, Shinjuku-ku, Tokyo 169, Japan
[2]Department of Materials Science and Engineering, Waseda University,
Ohkubo, Shinjuku-ku, Tokyo 169, Japan
[3]Department of Chemistry, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01, Japan
[4]Osaka Electro Communication University, Hatsucho, Neyagawa, Osaka 572, Japan
[5]Center for X-ray Optics Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

INTRODUCTION

X-ray transmission measurements give in general important information on chemical bonding or chemical reactivity because unoccupied molecular orbitals localized above valence bonds are characteristic of chemical species. If the number of emitted secondary electrons is proportional to the number of electron holes produced by incident X-rays, or the fluorescence X-ray is dominant in decay processes of the holes, the total electron yield (TEY) or fluorescence yield (FY) is a good measure of X-ray absorption. Then the transmission measurements are frequently replaced by TEY or FY experiments[1] due to simplicity of the latters. K edge absorption spectra obtained from light elements such as B, C, N, O and F are expected to have characteristic shapes of chemical compounds if chemical environments of the atoms of interest are different. In this investigation a series of oxides are studied to clarify their electronic structures experimentally and theoretically.

EXPERIMENTAL RESULTS

Experiments were carried out at ALS beamline 6.3.2. TEY spectra were recorded using pulverized specimens embedded in In foil. Surface of In was in general covered with its oxide and then gave a TEY spectrum, as shown in Fig. 1. Thickness of the specimens was chosen to be thick enough to avoid contamination of TEY from In foil, but to be thin enough to prevent surface charging of the specimen. Examples of TEY are shown in Fig. 2, which are characterized by easily distinguishable shapes even for the same metal oxides if valence states of the metal are different (PbO and PbO_2), and even for the same valence states if species of cations are different (Cr_2O_3 and Fe_2O_3). Such dramatic charge in spectral shapes is expected to be explained by the molecular orbital theory.
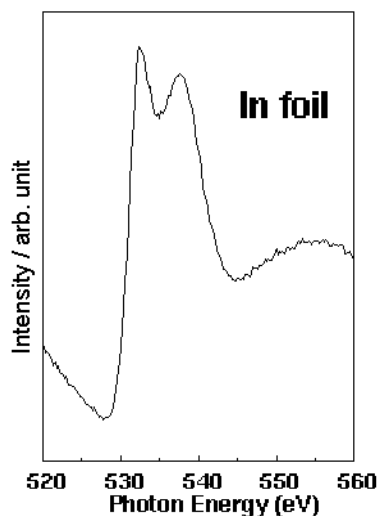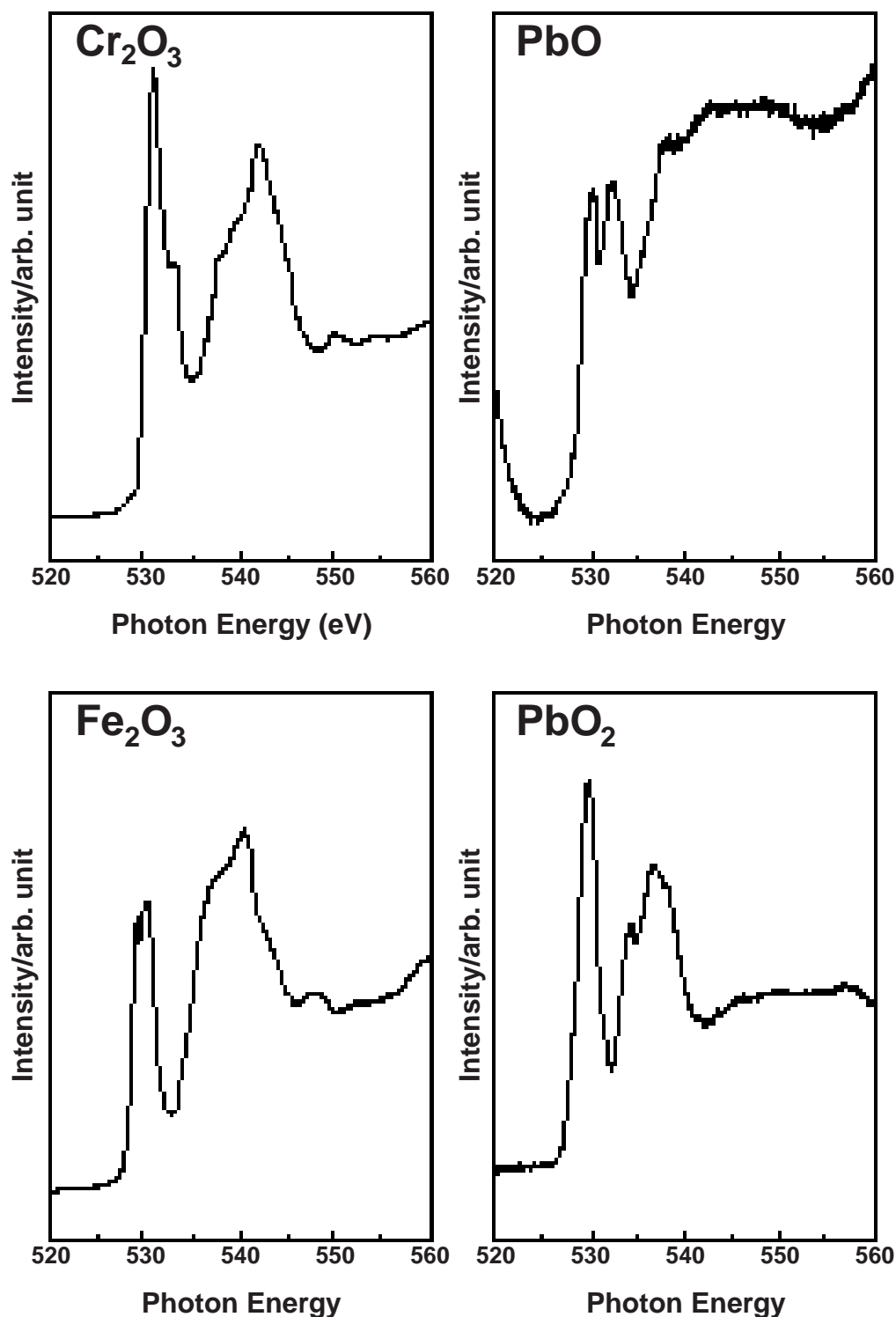

Fig. 1. TEY of In foil covered with its oxide

Fig. 2. TEY of Cr_2O_3, Fe_2O_3, PbO and PbO_2

MOLECULAR ORBITAL CALCULATION

Molecular orbital (MO) calculations were performed using the discrete-variational (DV) $X\alpha$ method[2,3] in which a linear combination of numerically generated atomic orbitals were used to describe the MOs. The basis functions for MgO were 1s~3p for O and Mg. Sample points of 2000 for numerical integration were distributed three-dimensionally in a manner described elsewhere[3]. A diameter and depth of the potential to confine wave functions were chosen to be $0.7a_0$ and

-3.0 Hartree, respectively where a_0 was an interatomic distance between O and Mg atoms. In the present study, a cluster model of $(Mg_6O_{19})^{26-}$ was employed, as shown in Fig. 3. If we assume that TEY or FY is described by photo-absorption originated from electronic excitation from O 1s to O 2p and 3p, an observed spectrum of TEY or FY near the O K edge for MgO, as shown in Fig. 4, can be explained approximately by unoccupied partial density of states (PDOS) of O 2p and 3p. The PDOS calculated here is compared with TEY and FY spectra in Fig. 4. This suggests that further discussions are indispensable whether or not the X-ray absorption can mostly be written by the dipole approximation. Comparison between observed TEY and calculated PDOS is in due course for several oxides.
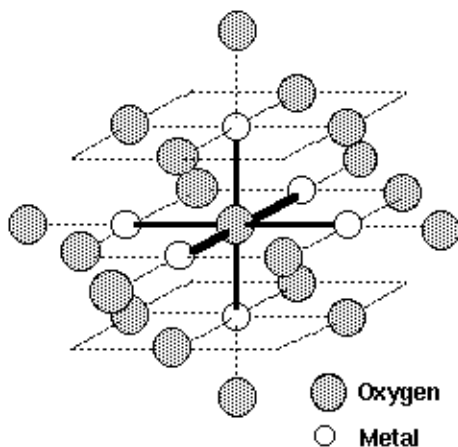

Fig.3. A $(Mg_6O_{19})^{26-}$ cluster used in DV-Xα calculation
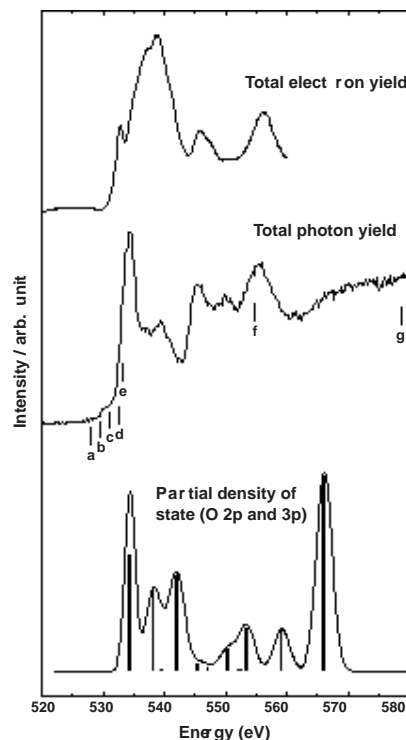

Fig. 4. Comparison among TEY, FY and PDOS for MgO

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Principal investigator: Masayuki Uda, Laboratory for Materials Science and Technology, Waseda University. Email: muda@mn.waseda.ac.jp.